OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0021

Technical Report No. 16

The Glass Transition Temperature as a Parameter for Monitoring the Isothermal Cure of an Amine-Cured Epoxy System

by

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February 1989

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1 REPORT NUMBER: Technical Report # 16	2 GOVT ACCESSION NO: N/A
3 RECIPIENT'S CATALOG NUMBER: N/A	
4 TITLE (and Subtitle): The Glass Transition Temperature as a Parameter for Monitoring the Isothermal Cure of an Amine-Cured Epoxy System	5 TYPE OF REPORT & PERIOD COVERED: 1/7/88 - 2/15/89
	6 PERFORMING ORG. REPORT NUMBER:
7 AUTHOR(s): G. Wisanrakkit, J. K. Gillham	8 CONTRACT OR GRANT NUMBER(s): N00014-84-K-0021
9 PERFORMING ORGANIZATION NAME AND ADDRESS: Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544	10 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:
11 CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Attn: Code 413, 800 N. Quincy St., Arlington, VA 22217	12 REPORT DATE: February 1989
	13 NUMBER OF PAGES: 28
14 MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15 SECURITY CLASS (of this report): Unclassified
	15a DECLASSIFICATION/DOWNGRADING SCHEDULE

16 DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

N/A

18 SUPPLEMENTARY NOTES

19 KEY WORDS (Continue on reverse side if necessary and identify by block number)

Cure, Vitrification, Glass Transition, Kinetics, Time-Temperature-Transformation Cure Diagram, Conversion, (mgm)

20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Torsional Braid Analysis (TBA) technique is a convenient one for monitoring the cure of thermosets in terms of the glass transition temperature (T_g) as well as the times to macroscopic gelation and to vitrification. In the process of cure T_g can rise from its initial value (T_{go}), through the value corresponding to its molecular gel point ($_{gel}T_g$), to that of the

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S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

fully cured material ($T_{g\infty}$). Differential Scanning Calorimetry (DSC) is also used to measure T_g, and is especially useful in relating T_g to conversion. These techniques have been used to investigate the feasibility of using T_g as the prime parameter for monitoring the complete cure process. The objective is attractive for systems in which there is a one-to-one relationship, independent of the cure temperature, between the T_g of the material and its chemical conversion. It follows for such systems, for example, that the chemical activation energy can be determined equivalently from both the times to reach a fixed conversion and the times to reach a fixed T_g. A simple methodology is presented for calculating the times for the material to achieve any attainable T_g (≡conversion) at different cure temperatures, and the times for its T_g to reach any cure temperature below $T_{g\infty}$ (i.e. vitrification). The results are presented in the form of a Time-Temperature-Transformation (TTT) cure diagram. The procedure requires knowledge of the activation energy and data points relating T_g-t_{cure}-T_{cure} over the entire range of T_g (for example, T_g versus time at $T_{cure}=T_{g\infty}$ from $T_g=T_{go}$ to $T_{g\infty}$). Preliminary results are presented for a tetrafunctional aromatic diamine/diepoxy system. The results show, in particular, that the reactions prior to vitrification are kinetically controlled.

THE GLASS TRANSITION TEMPERATURE AS A PARAMETER FOR MONITORING THE ISOTHERMAL CURE OF AN AMINE-CURED EPOXY SYSTEM

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ABSTRACT

The Torsional Braid Analysis (TBA) technique is a convenient one for monitoring the cure of thermosets in terms of the glass transition temperature (T_g) as well as the times to macroscopic gelation and to vitrification. In the process of cure T_g can rise from its initial value (T_{go}), through the value corresponding to its molecular gel point ($_{gel}T_g$), to that of the fully cured material ($T_{g\infty}$). Differential Scanning Calorimetry (DSC) is also used to measure T_g, and is especially useful in relating T_g to conversion. These techniques have been used to investigate the feasibility of using T_g as the prime parameter for monitoring the complete cure process. The objective is attractive for systems in which there is a one-to-one relationship, independent of the cure temperature, between the T_g of the material and its chemical conversion. It follows for such systems, for example, that the chemical activation energy can be determined equivalently from both the times to reach a fixed conversion and the times to reach a fixed T_g. A simple methodology is presented for calculating the times for the material to achieve any attainable T_g (≡conversion) at different cure temperatures, and the times for its T_g to reach any cure temperature below $T_{g\infty}$ (i.e. vitrification). The results are presented in the form of a Time-Temperature-Transformation (TTT) cure diagram. The procedure requires knowledge of the activation energy and data points relating T_g-t_{cure}-T_{cure} over the entire range of T_g (for example, T_g versus time at $T_{cure}=T_{g\infty}$ from $T_g=T_{go}$ to $T_{g\infty}$). Preliminary results are presented for a tetrafunctional aromatic diamine/diepoxy system. The results show, in particular, that the reactions prior to vitrification are kinetically controlled.

INTRODUCTION

The glass transition temperature, T_g, is a sensitive and practical parameter for following cure of reactive thermosetting systems. A wide range of values of T_g is encountered during cure, and it can be measured easily throughout the entire range of cure. The fact that T_g increases nonlinearly with conversion in crosslinking systems makes it even more sensitive in the later stages of reaction. Sensitivity is needed especially when the reaction rate is low, for example at high conversion and after solidification (vitrification).

A convenient summary of the changes which occur during cure of a thermosetting system is the isothermal time-temperature-transformation (TTT) cure diagram. The diagram, schematically shown in Figure 1, displays the states of the material and characterizes the changes in the material during isothermal cure as a function of time [1-3]. Material states include liquid, sol glass, sol/gel rubber, gel rubber, sol/gel glass, gel glass and char. The various changes occuring in the material during isothermal cure are characterized by contours of the times to reach those events. Relevant contours include: molecular gelation (corresponding in simple systems to the unique conversion at the molecular gel point), vitrification (corresponding to T_g rising to the cure temperature), devitrification (corresponding to T_g decreasing to T_{cure} because of thermal degradation), and char formation (corresponding to T_g increasing to T_{cure} because of thermal degradation). The progress of the isothermal cure process and the state of the material can be clearly summarized in terms of these contours in the TTT diagram.

T_g is an important and useful parameter in the TTT cure diagram. For example, for vitrification, devitrification and char formation, T_g equals T_{cure}. The molecular state of the unreacted material has $T_g=T_{go}$, and that of the fully reacted material has $T_g=T_{g\infty}$. Molecular gelation corresponds to a definite chemical composition for which $T_g=_{gel}T_g$. Macroscopic gelation (corresponding, for example, to an isoviscous state) occurs simultaneously with

vitrification at $T_{cure}=T_g=gel T_g$'.

The basic parameter governing the state of the material is the chemical conversion. Therefore, more details of the cure process can be visualized by incorporating iso-conversion contours in the TTT diagram. The purpose of this present work is to study the feasibility of using T_g as a direct one-to-one measure of chemical conversion, and to demonstrate a simple methodology for constructing iso-T_g contours and the vitrification curve in the isothermal TTT diagram from T_g versus time data at different values of T_{cure}, provided that a one-to-one relationship between T_g and conversion exists [4].

CHEMICAL SYSTEM AND EXPERIMENTAL PROCEDURE

The system chosen for this study is a diglycidyl ether of bisphenol A (DER337, Dow Chemical Co.) cured with a stoichiometric amount of a tetrafunctional aromatic diamine, trimethylene glycol di-p-aminobenzoate (TMAB,Polaroid Corp) (Fig. 2). The solution of the reactants (~1g/1ml) was formed by adding the amine to the solution of epoxy in methyl ethyl ketone (MEK) at room temperature. MEK was later removed prior to each experiment by holding each small specimen (~25 mg) at 70°C for 2 hours in an inert atmosphere. The mixture, after the removal of MEK, was taken as the initial (uncured) state of the system. This procedure was adopted in order to avoid the necessity of mixing the reactants at high temperature. TMAB is a highly crystalline solid with a melting point of 125°C and DER337 is a highly viscous liquid at room temperature. (Without the use of solvent, TMAB must first be melted and then mixed with the epoxy above 125°C in order to ensure uniform mixing. This can lead to substantial conversion of the initial mixture.)

Two complementary techniques were used in this study: Differential Scanning Calorimetry (DSC) and Torsional Braid Analysis (TBA). A Perkin-Elmer instrument (DSC-4) was used to measure T_g and the heat evolution of the reaction, from which T_g vs. the fractional extent of chemical conversion was determined. Samples were partially cured in DSC aluminum pans in an oven at three different temperatures (136, 150 and 160°C) under

N_2 flow. After cure times ranging from 15 minutes to 6 hours, samples were removed from the oven, allowed to free cool to room temperature, and then scanned in the DSC unit from -20°C to 350°C at 5°C/min to determine T_g and the residual exotherm (ΔH_R) to complete the reaction. (The scan rate of 5°C/min was used because at higher scan rates, the sample began to degrade at high temperatures before the reaction was fully completed). T_g appears as an endothermic step change over an interval of temperature in a DSC scan. In this study, T_g was taken as the mid-point of the transition interval. The total heat of reaction (ΔH_T) was also determined in the same way by scanning uncured samples. The extent of reaction,α, was quantitatively calculated as [5] $\alpha = (\Delta H_T - \Delta H_R)/\Delta H_T$. Figure 3 shows the DSC trace of an uncured sample. The apparent total heat of reaction was found to be 90 cal/gm of mixture, and the initial glass transition temperature, T_{go}, was 0°C. The glass transition temperature of the fully reacted sample, $T_{g\infty}$, taken as the highest value of T_g, obtained at 150°C and 160°C after extended cure times, was 145°C.

In this study, TBA was used to measure directly the times to macroscopic gelation and vitrification during isothermal cure at different temperatures, and the T_g of the material versus time at different temperatures. In the TBA experiment, the specimen is intermittently activated into free torsional oscillation to generate a series of damped sine waves, from which two mechanical parameters, namely, relative rigidity and logarithmic decrement, are determined. After impregnateing a heat-cleaned glass braid with the solution of the reaction mixture, mounting the specimen at room temperature, and heating at 70°C for 2 hours, the temperature was raised at 10°C/min to the cure temperature and held at the cure temperature for a definite time. The TBA spectrum during prolonged isothermal cure yielded two important parameters, namely, the time to macroscopic gelation and the time to vitrification. They appeared as two successive maxima in the logarithmic decrement versus time of cure (Fig. 4A).

After the isothermal cure, the TBA specimen was control-quenched at 10°C/min to -50°C and then scanned from -50°C to 250°C at 1°C/min to obtain the T_g attained by the

particular isothermal cure. A subsequent scan from 250°C to -50°C at 1°C/min gave the maximum glass transition temperature, $T_{g\infty}$, of the material. All T_g's were identified by the maxima of the peaks of the logarithmic decrement spectra (0.9 Hz.) (Fig. 4B. Note that the lower temperature limit in the figure is -180°C in order to display a cryogenic secondary transition). With this definition, T_g could be specified easily and unambiguously.

The TBA technique provides a useful means of monitoring the cure in terms of these measured parameters, (i.e., T_g, macroscopic gel times, vitrification times), and provides a convenient way of directly constructing an experimental isothermal TTT cure diagram for the system from the times to gelation and to vitrification vs. isothermal temperature.

T_{go} and $T_{g\infty}$ determined by the TBA technique for this system were 10°C (0.9 Hz.) and 156°C (0.9 Hz), respectively. There was a difference of about 10°C between the value of T_g determined by the DSC and TBA techniques. This difference was expected because of the difference in the operational definitions of T_g, the difference in the measuring time scale (the frequency used in TBA is ~1 Hz.), the differences in the procedures of initial heating to and subsequent cooling from the isothermal temperature, and the difference in the temperature scanning rates during measurement.

The T_g versus time data obtained by the TBA technique are used in the calculation of the iso-T_g and vitrification contours, although the calculation can also be done entirely using the DSC results.

There are advantages, however, in using TBA versus DSC for measuring T_g:

(a) For TBA, T_g is a prominent transition and can be measured accurately because the maximum of the logarithmic decrement can be located easily and unambiguously . For DSC the T_g is a weak transition and is measured from an endothermic shift in the specific heat versus temperature curve;

(b) The slow temperature scan rate (1°C/min) in the TBA technique provides good temperature resolution of the resulting spectra, such that T_g can be determined to within 1°C. In comparison, the DSC technique requires a reasonably high temperature scan rate (5-

20°C/min) in order to detect T_g, which therefore reduces the resolution of the data;

(c) The TBA technique gives the same value of T_g by either scanning up or scanning down in temperature during measurements, whereas the DSC technique gives substantially different values because of a problem which is inherent to the instrument;

(d) In the TBA technique, the physical aging effect on T_g is essentially removed before T_g is identified by the maximum in the logarithmic decrement during a heating scan [6]. In contrast, in the DSC technique, the effect of prior physical annealing and the onset of reaction exotherm can directly affect the T_g measurement.

RESULTS AND DISCUSSIONS

DSC RESULTS

Conversion versus Cure Time

Figure 5 shows the extent of reaction,α, as a function of cure time for three isothermal cure temperatures (136, 150 and 160°C) under conditions far from diffusion control (due to vitrification). The results for high conversion (α> 95%) are not available because the residual exotherm becomes too small to be measured accurately by the DSC. It is clear that the DSC technique is not sensitive enough to monitor high conversions. However, curing at 150°C and 160°C for extended times raises T_g to its maximum value even though the change in conversion in the later stages is not measurable by the DSC (e.g. for T_{cure} 150°C/time 9 hr, T_g= 145°C $\equiv T_{g\infty}$). Therefore, ΔH as measured is underestimated.

The data in Figure 5 can be used to calculate the activation energy for the reaction. In the usual manner, the kinetic rate law can be expressed as

$$\frac{d\alpha}{dt} = k\, f(\alpha) = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

where α = the extent of reaction

k = reaction rate constant which is assumed to be temperature dependent through the Arrhenius relationship

$f(\alpha)$ = a function of reactant concentration

A,E_a, and R have their usual meanings in the Arrhenius equation.

T is the cure temperature in degrees Kelvin.

Rearranging equation (1) and integrating,

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A \exp\left(-\frac{E}{RT}\right) t_\alpha \qquad (2)$$

where t_α is the time at which the conversion reaches α. Taking the natural logarithm

$$\ln\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) = \ln(A) - \frac{E}{RT} + \ln(t_\alpha)$$

$$\ln(t_\alpha) = \frac{E}{RT} + \left[\ln\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) - \ln(A)\right] \qquad (3)$$

For a fixed conversion, the last term in the brackets is a constant. Plotting the natural logarithm of the time to reach a fixed conversion, t_α, versus the reciprocal cure temperature should yield a straight line, the slope of which can be used to calculate the activation energy of the reaction. The times to reach fixed fractional conversions (0.30, 0.40, 0.50 and 0.60) at the three cure temperatures were determined from the curves in Figure 5 and are plotted against the reciprocal cure temperature in Figure 6. All plots appear to be parallel straight lines, the slopes of which yield the activation energy for the reaction (14.91, 14.95, 15.28 and 14.45 Kcal/mole, respectively). The average activation energy is 14.9 Kcal/mole.

First-order Reaction Kinetics

It has been found that the reaction kinetics in the early stages of the isothermal curing (prior to vitrification) of several amine-cured epoxy systems can be described by first order kinetic rate law [3,7]. For all of the present DSC data, the material had not vitrified during isothermal cure, i.e. $T_g < T_{cure}$. Treating the reaction as if it obeys first-order kinetics and assuming that the only reaction occuring in the system involves only one

epoxy group reacting with one amine hydrogen atom without distinguishing the reactivities of the primary and secondary amino hydrogens, the reaction rate is given by

$$\frac{d\alpha}{dt} = k(1-\alpha)$$

where α is the extent of reaction.

Upon integration, $\ln(1-\alpha) = -kt$.

The DSC conversion data are plotted in Figure 7 according to these assumptions. It is apparent for this system that simple first-order kinetics can only represent the data in the initial stages of the reaction. It is not applicable at high conversion even in the absence of isothermal vitrification (which could lead to diffusion control of the reactions).

The initial apparent rate constant at each temperature can be determined from the slope of the straight line in Figure7. The results are plotted against the reciprocal temperatures in the Arrhenius fashion in Figure 8. The reaction activation energy under the assumed first-order kinetics is 14.52 Kcal/mol.

T_g versus Conversion

Figure 9 shows a plot of T_g versus conversion for all data at the three cure temperatures from the DSC data. All data appear to fall on a single curve. Thus, it is quite clear that there is a one-to-one relationship between T_g and the chemical conversion independent of the cure temperature (for the limited range of ΔT=24°C). These results are in agreement with the work done by other investigators [8,9]. (However, it has been observed in Ref. 6 that the T_g of the material after vitrification depends on both conversion and physical aging. This can affect the relationship between T_g and conversion.)

Furthermore, it is noted that T_g is a nonlinear function of conversion; it rises more at high conversion[3,6,10]. An explanation accounting for this nonlinear behavior is that T_g is more strongly dependent on the concentration of the highest-functional crosslinking units (i.e. for this system, tetrafunctional amines with all four of the amino hydrogens reacted) than that of the lower-functional crosslinking units (i.e. amines with only three amino hydrogens reacted). Since the concentration of the higher-functional crosslinking

units increases at high conversion at the expense of the lower functional crosslinking units [11], T_g rises more appreciably at high conversion with small changes in the overall conversion. As a consequence of this nonlinear behavior, T_g is sensitive to changes in conversion in the later stages of cure when the changes are small due to low reactant concentration at high conversion.

Furthermore, the sensitivity of T_g to conversion and the advantage of the accuracy for measuring T_g, make T_g a promising candidate for monitoring the slow rate of cure in the diffusion controlled regime. Segmental diffusion mechanisms dominate the reaction especially when T_g rises above T_{cure} [3, 12,13] and can drastically slow down the reaction even at low conversion for low cure temperatures. The possibility of using the changes in the T_g of the system to monitor the reaction under diffusion controlled kinetics is the subject of our current research.

It is noted that for systems with unequal reactive functional groups, different temperature cure paths may result in the final materials with the same chemical conversion but different chemical structures. This is because the relative reactivities of the functional groups can change with the reaction temperatures. In reacting epoxy with aromatic amine, the primary amino hydrogen may react much faster than the secondary amino hydrogen [14-17]. Therefore, it is conceivable for the current epoxy/amine system that the general one-to-one relationship between Tg and conversion may be affected by different cure temperatures. However, the present DSC results (with curing temperature spread of 24°C) do not suggest this effect. If the reaction rate for the primary amino hydrogen is much greater than that for the secondary amino hydrogen, then prior to gelation, the reaction involves mainly primary amino hydrogens reacting with epoxy groups which results in chains with no crosslinks. After gelation, most of the primary amino hydrogens will have reacted, and the remaining secondary amino hydrogens of the diamine will have essentially the same reactivity. Further conversion involves primarily the reaction between epoxy groups and secondary amino hydrogens to form trifunctional and tetrafunctional branch points.

Consequently, the one-to-one relationship between Tg and conversion is unaffected by the unequal reactivity of the primary and secondary amino hydrogens, even though the material reacts at different temperatures. The validity of this hypothesis will be tested by expanding the range of T_{cure} to be investigated.

TBA RESULTS

T_g vs. Cure time

Figure 10 shows the progression of T_g as functions of cure time for five different isothermal cure temperatures (130, 140, 150, 160, and 200°C). These temperatures are greater than $T_{g\infty}$ minus 30°C. It is expected in this temperature range that the T_g of the material can eventually achieve $T_{g\infty}$ given long enough cure time. It can be seen from the results that T_g increases at a rapid rate until its value rises to the cure temperature (i.e. vitrification). In the vicinity of T_g greater than T_{cure} for cure temperatures below $T_{g\infty}$(=156°C), T_g increases at a much slower rate which is an indication that the reaction is becoming diffusion controlled. Nevertheless, changes (chemical and/or physical) do occur slowly in the material beyond vitrification.

Determination of Reaction Activation Energy

From the DSC results (for limited ΔT_{cure} =24°C), it appears that there is a one-to-one relationship between T_g and the reaction conversion. It is therefore possible to consider conversion as a unique function of T_g, (i.e.$\alpha = f(T_g)$). Consequently, the times to reach a fixed T_g is equivalent to the times to reach a fixed conversion. Therefore, the activation energy of the reaction can be determined from the data in Figure 10 in the same way as the calculation using the conversion data.

The times to reach different T_g's (60, 70, 80, 90 and 100°C), determined from the TBA data in Figure 10, are plotted versus the reciprocal cure temperatures in Figure 11. The range of these T_g's is chosen such that the material is far from isothermal vitrification

for the cure temperature (i.e. $T_g << T_{cure} \geq 130°C$). All plots can be well correlated with straight lines. The slope of each line gives an activation energy for the reaction. (The results are 15.46, 15.28, 15.41, 15.14, and 15.01 Kcal/mole, respectively.) The average value is 15.3 Kcal/mole. The average value of the activation energy obtained in this way is close to that found using the times to reach a fixed conversion for different cure temperatures from the DSC data (recall E_a=14.9 Kcal/mole from DSC). These results indicate that for this system, the use of T_g as an index of changes in chemical conversion is valid.

Also included in Figure 11 is a plot of $\ln(t_{gel})$, the time to reach the macroscopic gelation peak in the logarithmic decrement curve in the isothermal TBA scan, versus the reciprocal cure temperature. The resulting plot can also be correlated with a straight line. However, the activation energy determined from the slope of this line is 13.7 Kcal/mole which is significantly different from the values determined from iso-T_g or iso-conversion data. According to the theory of gelation for a unireaction system by Flory [18], the onset of molecular gelation occurs at a fixed conversion for all cure temperatures, and therefore, the times to reach molecular gelation for such systems should be the same as the times to reach the fixed conversion corresponding to molecular gelation (and equivalently, to the times to reach the fixed T_g, $_{gel}T_g$). The fact that the activation energy determined from the times to reach the macroscopic gelation peaks of the TBA scan is different from those determined from iso-T_g and iso-conversion data suggests that the macroscopic gelation peak does not correspond to molecular gelation. The macroscopic gelation relaxation may be an iso-viscous event. The Arrhenius plot of the log time to any iso-viscous event versus 1/T yields an apparent viscous activation energy, which is less than the activation energy for the reaction [1]. (The viscous activation energy approaches the value for the chemical activation energy leading to gelation only if the level of the viscosity of the observed event is infinitely high[1].)

Construction of the Vitrification Contour and Iso-T_g contours in the TTT Diagram[4]

(a) Iso-T_g Contours

The reaction activation energy determined in the previous section can be used for constructing an iso-T_g contour if, in addition, a data point on the contour is known.

From the integral form of the rate expression,

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A \exp\left(-\frac{E}{RT}\right) t_{\alpha}$$

The left hand side of the equation is only a function of conversion, α, and thus, also a function of T_g only [$\equiv F(Tg)$]. The time to reach a fixed conversion, t_{α}, can be replaced by the time to reach a fixed T_g, t_{Tg}. Thus, the above equation can be written as

$$F(T_g) = A \exp\left(-\frac{E}{RT}\right) t_{T_g}$$

This equation is valid for all cure temperatures as long as the reaction mechanism remains kinetically controlled and does not change with the cure temperature.

Let $t_{Tg,1}$ be the time needed to reach a given T_g at cure temperature T_1 and let $t_{Tg,2}$ be the time needed to reach the same T_g at cure temperature T_2.

Then, from equation (3) above,

$$F(T_g) = A \exp\left(-\frac{E}{RT_1}\right) t_{T_g,1}$$

and

$$F(T_g) = A \exp\left(-\frac{E}{RT_2}\right) t_{T_g,2}$$

For a fixed T_g, the two equations above are equal.

$$A \exp\left(-\frac{E}{RT_1}\right) t_{T_g,1} = A \exp\left(-\frac{E}{RT_2}\right) t_{T_g,2}$$

Taking the natural logarithm gives

$$-\frac{E}{RT_1} + \ln(t_{T_g,1}) = -\frac{E}{RT_2} + \ln(t_{T_g,2}) \qquad (4)$$

Equation (4) provides a relationship between the times to reach a fixed T_g and the corresponding cure temperatures. Thus if a time to reach a particular T_g at a cure

temperature (i.e.$t_{Tg,1}$ at T_1) is known, then the times to reach the same T_g at different temperatures (i.e.$t_{Tg,2}$ at T_2) can be calculated from equation (4) provided that the reaction activation energy is available.

In the calculation of an iso-T_g contour, the reaction activation energy calculated from the TBA times to reach T_g of 70°C (E_a= 15.3 Kcal/mole) is used because this T_g is greater than 40°C below all isothermal vitrification temperatures in the experiment, and therefore up to this point, the reactions are expected to be primarily kinetically controlled. The calculated results are incorporated into the TTT diagram in the form of a series of iso-T_g contours, by plotting the cure temperatures against the logarithm of the times to reach a particular T_g. The known data point ($t_{Tg,1}$ at T_1) for each iso-T_g contour is obtained from the interpolated data of the T_g versus t_{cure} curve at 150°C in Figure 10. Figure 12 shows the calculated iso-T_g contours (from T_g= 12°C to T_g= 155°C). The figure also shows selected experimental iso-T_g data obtained from interpolating the curves in Figure 10 for T_{cure} =130, 140, 160 and 200°C. The calculation appears to correlate well with the experimental data (the range of T_{cure} extends beyond the ΔT_{cure} used for α vs. T_g). These results show that for the cure temperature range in the experiment, the reactions prior to vitrification are mainly kinetically controlled. Data from the macroscopic gelation peaks are also included in Figure 12. The macroscopic gelation curve appears to lie close (but not parallel) to the iso-T_g= 70°C line. From a practical point of view, one can visualize the degree of curing and the state of chemical conversion through the levels of these iso-T_g contours .

(b) Vitrification Curve

The curing reaction of thermosets in general will be a combination of chemical kinetic and intersegmental diffusion controls [12,13]. However, it has been found in our previous work [3,19] and by other investigators [20] that for the curing of epoxy-amine system, the reaction is primarily kinetically controlled with a single constant activation energy up to the vicinity of vitrification. Therefore, the iso-T_g relation (equation 4) is valid until the material vitrifies and can be used to estimate the isothermal times to vitrification. On the iso-T_g curve (equation 4), a point will correspond to a vitrification point when T_2=T_g.

Graphically, this is equivalent to locating the point where the horizontal line at $T=T_{cure}$ intersects the iso-$T_g=T_{cure}$ line. The resulting points from all possible iso-T_g contours (from iso-$T_g=T_{go}$ to iso$T_g=T_{g\infty}$) constitute the vitrification curve in the TTT diagram. The calculated vitrification curve is shown in Figure 12 together with the vitrification points which were determined experimentally from the second maximum in the logarithmic decrement of the TBA isothermal scans for different T_{cure}'s (110, 120, 130, 140 and 160°C). The calculated curve agrees with the experimental results. Thus, neglecting diffusion control prior to vitrification does not significantly affect the calculation of the time to vitrify.

Previous approaches to calculation of the time to vitrification require analytical knowledge of both the kinetic rate law and the empirical relationship between T_g and conversion. [2,21]. The former relationship is quite complicated and difficult to obtain accurately. In those attempts, the conversion at vitrification (when $T_g=T_{cure}$) was obtained from the relationship between T_g and conversion. Once the conversion at T_g was known, then the time to vitrification was determined from an assumed kinetic rate law. All calculations also assumed a kinetically controlled reaction and one temperature-independent reaction mechanism. Thus, the present approach using the iso-T_g contours to determine the time to vitrification is considered more direct, less complicated, and can be more accurate than the previous ones. It treats T_g as a direct measure of conversion, and thus eliminates the error associated with relating T_g to conversion at vitrification. It relies on the measurement of T_g which can be done more accurately than the measurement of conversion.

Moreover, the procedure greatly simplifies the theoretical construction of the vitrification curve because it does not require knowledge of the kinetic rate law or the relationship between T_g and conversion (as long as it is one-to-one). The only required information is the reaction activation energy and some isolated data points, each of which relates a particular T_g, say T_g^*, to cure time at some cure temperature. Each datum point together with the activation energy yields an iso-$T_g=T_g^*$ line, from which vitrification point

can be determined for $T_{cure}=T_g^*$. If the whole vitrification curve is desired, data points relating T_g-t_{cure}-T_{cure} over the whole range of T_g from T_{go}, to $T_{g\infty}$ are required. This can be accomplished by following the progress of the T_g of the material as a function of cure time at a cure temperature close to $T_{g\infty}$ (preferably $>T_{g\infty}$ to avoid vitrification) over the course of cure. Then, data points relating the whole range of T_g with cure time at one cure temperature are available.

CONCLUSIONS

1) T_g is an appropriate parameter for monitoring the cure process for the following reasons:

a) T_g is easily measured by several techniques. (TBA is an especially convenient and sensitive one.)

b) T_g can be measured over the entire range of conversion from the unreacted state up to full conversion, (cf., viscosity which can only be measured up to gelation).

c) The results show that T_g for this epoxy-amine system is a function of conversion for the Tcure range investigated (ΔTcure = 24°C). The generality of this conclusion remains to be proven for wider cure temperature range.

d) The nonlinear dependence of T_g on conversion renders T_g more sensitive than other parameters (such as the heat of reaction and IR absorption bands of reactants and products) to the small changes in conversion with time when the reactant concentrations are low (i.e. kinetically limited at high conversion).

2) The same reasons mentioned above also make T_g an appropriate parameter for monitoring the slow reaction rate in the diffusion controlled region beyond vitrification (subject under current investigation.)

3) The times to reach a fixed conversion plotted against the reciprocal of the cure temperatures in an Arrhenius fashion can be used for determining the activation energy of the reaction, the value of which agrees well with that found from the times to reach a fixed

conversion. This supports the one-to-one relationship between T_g and conversion.

4) A simple methodology for constructing iso-T_g contours and the vitrification curve in the TTT diagram is presented. The basis of the approach is an assumed one-to-one relationship between T_g and conversion, and that kinetically controlled reaction dominates up to vitrification.

5) The results show that neglecting diffusion control prior to vitrification does not significantly affect the calculation of the vitrification curve. Thus, the reaction kinetics up to vitrification is primarily kinetically controlled.

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FIGURE CAPTIONS

Figure 1: A generalized isothermal time-temperature-transformation (TTT) cure diagram for a thermosetting system, showing critical temperatures (i.e. T_{go},$T_{g\infty}$, gelT_g), states of the material, and contours characterizing the setting process. The full cure contour corresponds to T_g=$T_{g\infty}$. The transition region corresponds to $T_{cure} \leq T_g < \sim(T_{cure}+40°C)$. Isoviscous contours in the liquid region correspond to fixed viscosity levels. For systems that undergo phase separation, this occurs prior to gelation.

Figure 2: Chemical system.

Figure 3: DSC scan of the initial uncured D.E.R.337/TMAB systemfrom -20°C to 350°C at 5°C/min to determine the initial glass transition temperature (T_{go}) and the total

heat of reaction (ΔH_t). Prehistory: heated at 70°C for 2hr and free cooled to room temperature.

Figure 4: TBA Dynamic mechanical spectrum of the system (DER337/TMAB) (A) during isothermal cure at 110°C for 26 hours: (+) relative rigidity, (•) logarithmic decrement. The two successive maxima in the logarithmic decrement are assigned as macroscopic gelation and isothermal vitrification, respectively; (B) during the sequential temperature scans (a,b and c) at 1°C/min: a (+,•) 110°C to -180°C, b (o,Δ) -180°C to 250°C, and c (+,•) 250°C to-180°C. (For other TBA data in this work, the lower temperature limit was -50°C).

Figure 5: DSC results. Fractional conversion versus time at different isothermal temperatures (136, 150 and 160°C).

Figure 6: DSC results. Arrhenius plots of ln (time to reach fixed conversion) (from Figure 5) versus 1/T (K) to determine the activation energy for the reaction.

Figure 7: DSC results. Conversion data plotted according to first-order kinetics. The reaction rate constant at each temperature is determined from the slope of each straight line.

Figure 8: DSC results. Arrhenius plots of the reaction rate constants determined from Figure 7.

Figure 9: T_g versus fractional conversion from the DSC results.

Figure 10: The progress of T_g as a function of time at different cure temperatures (TBA results).

Figure 11: Arrhenius plots of ln time to reach fixed T_g values and ln time to reach macroscopic gelation versus 1/T (K) (TBA results). Note $T_g << T_{cure} \geq 130°C$

Figure 12: Summary TTT cure diagram for DER337/TMAB, showing the calculated iso-T_g and vitrification contours (solid lines) (calculated from T_g vs t_{cure} at 150°C and the activation energy from time to T_g=70°C), and selected experimental iso-T_g data (x)(from T_g vs t_{cure} at T_{cure} = 130,140,160 and 200°C), vitrification data(■), and macroscopic gelation (▲) data.

THE THERMOSETTING PROCESS: TIME-TEMPERATURE-TRANSFORMATION ISOTHERMAL CURE DIAGRAM

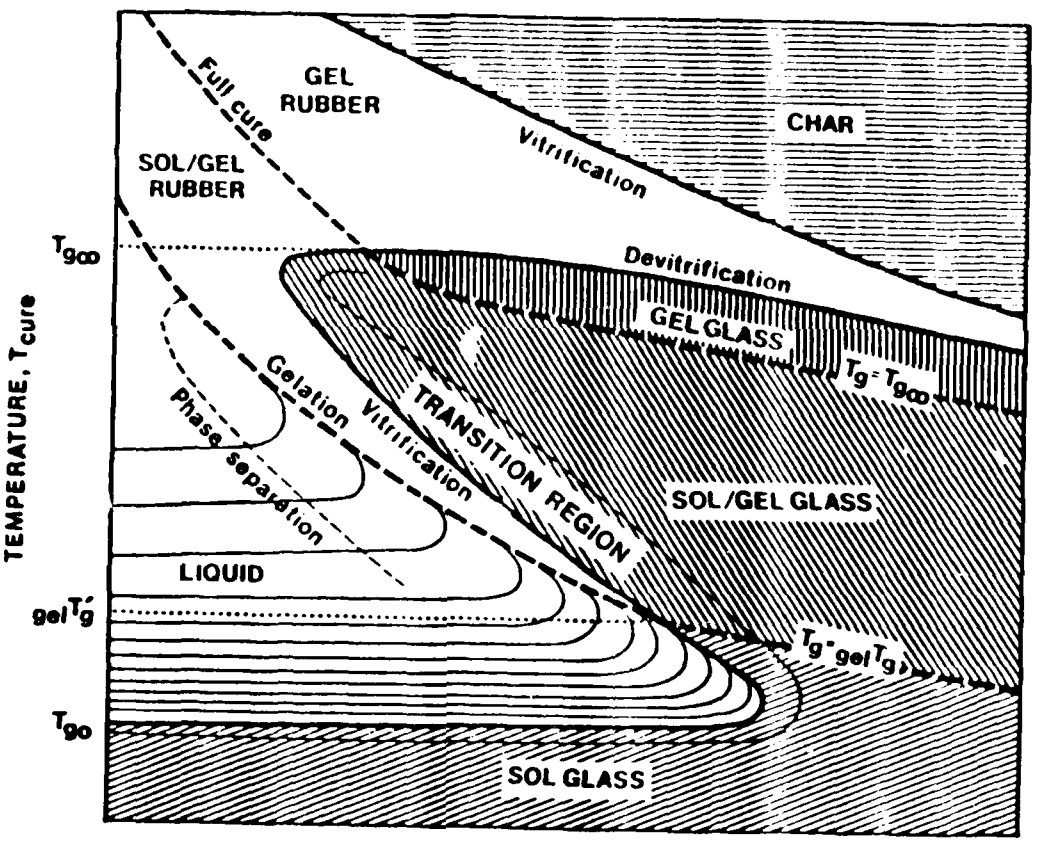
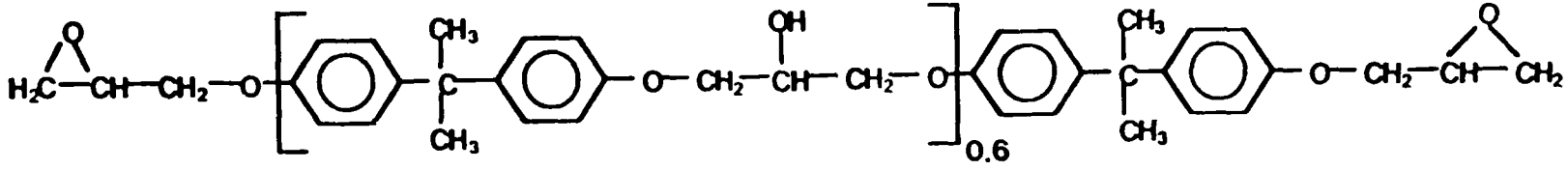
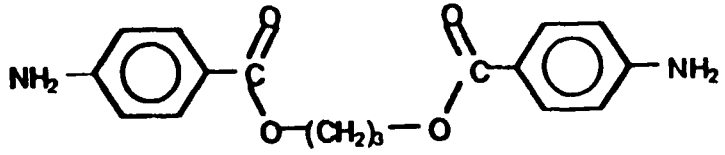


FIGURE 1

REACTANTS



Diglycidyl Ether of Bisphenol A (DER 337)



Trimethylene Glycol Di-p-aminobenzoate (TMAB)

FIGURE 2

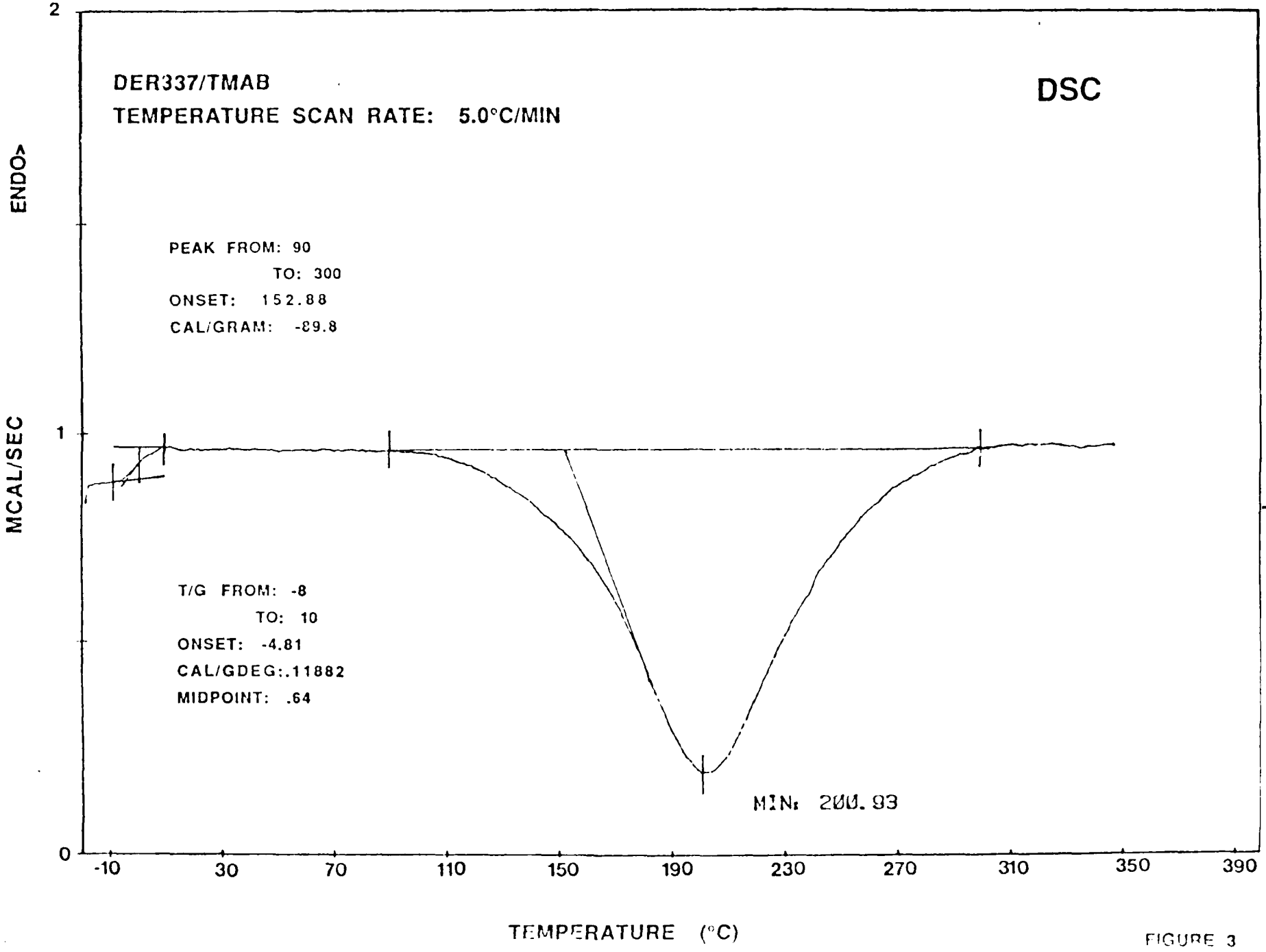

DER337/TMAB
TEMPERATURE SCAN RATE: 5.0°C/MIN
DSC
ENDO>
MCAL/SEC
2
1
0
PEAK FROM: 90
TO: 300
ONSET: 152.88
CAL/GRAM: -89.8
T/G FROM: -8
TO: 10
ONSET: -4.81
CAL/GDEG:.11882
MIDPOINT: .64
MIN: 200.93
-10
30
70
110
150
190
230
270
310
350
390
TEMPERATURE (°C)

FIGURE 3

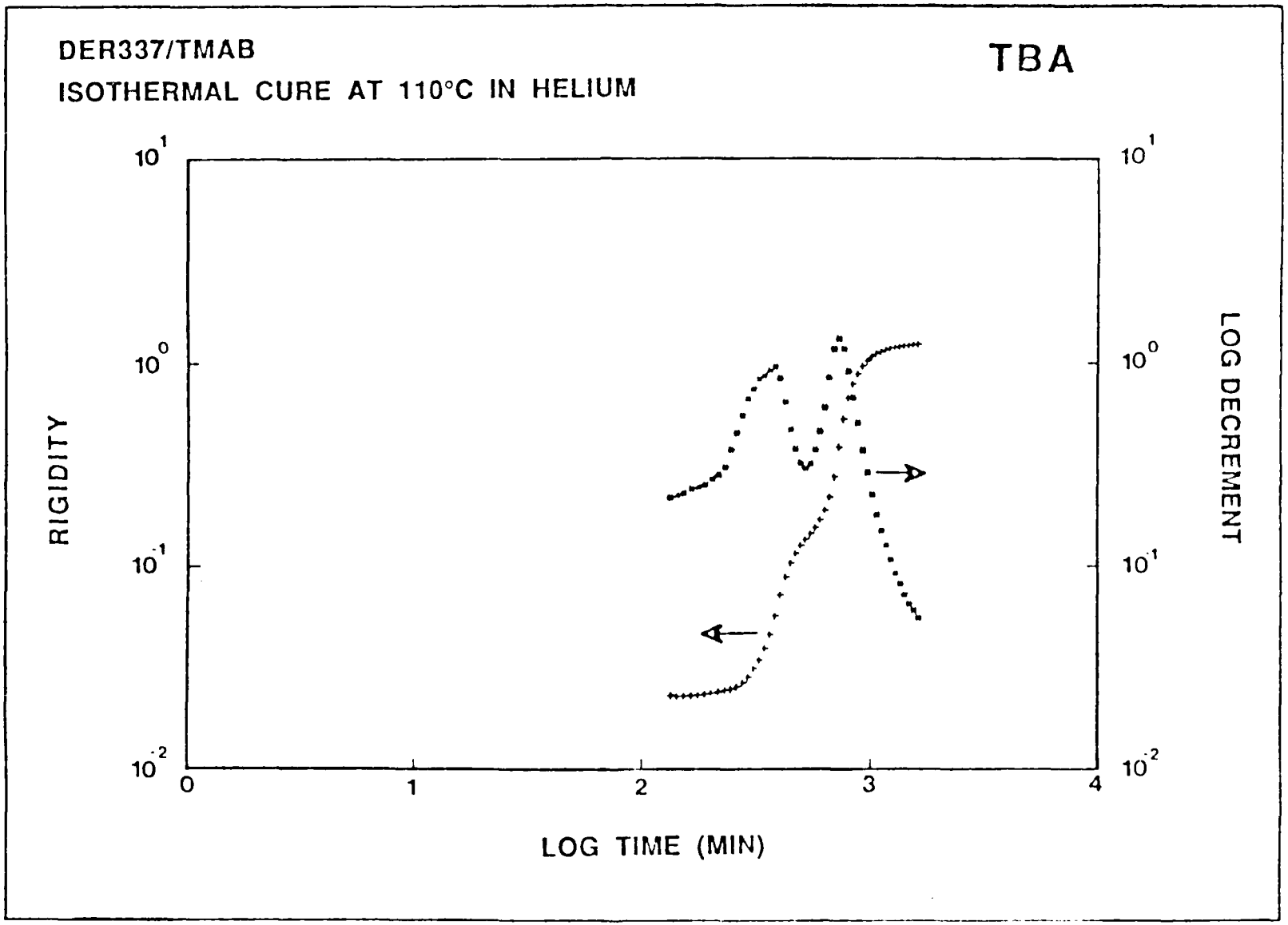

DER337/TMAB
ISOTHERMAL CURE AT 110°C IN HELIUM
TBA
RIGIDITY
LOG DECREMENT
LOG TIME (MIN)
10^1
10^0
10^-1
10^-2
0
1
2
3
4

FIGURE 4A

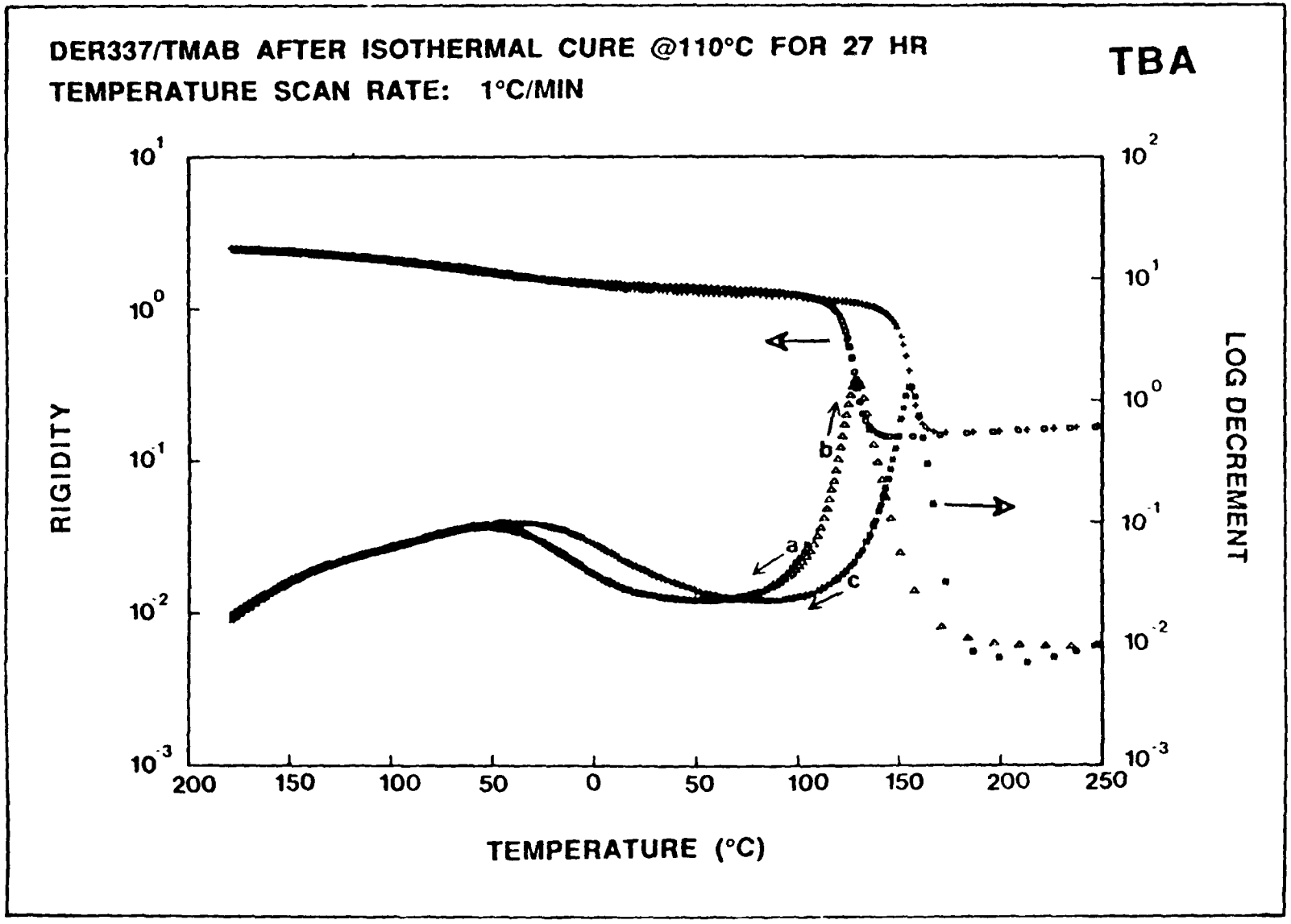

DER337/TMAB AFTER ISOTHERMAL CURE @110°C FOR 27 HR
TEMPERATURE SCAN RATE: 1°C/MIN
TBA
RIGIDITY
LOG DECREMENT
TEMPERATURE (°C)
a
b
c
10^1
10^0
10^-1
10^-2
10^-3
10^2
200
150
100
50
0
50
100
150
200
250

FIGURE 4B

CONVERSION VS. TIME [DSC]

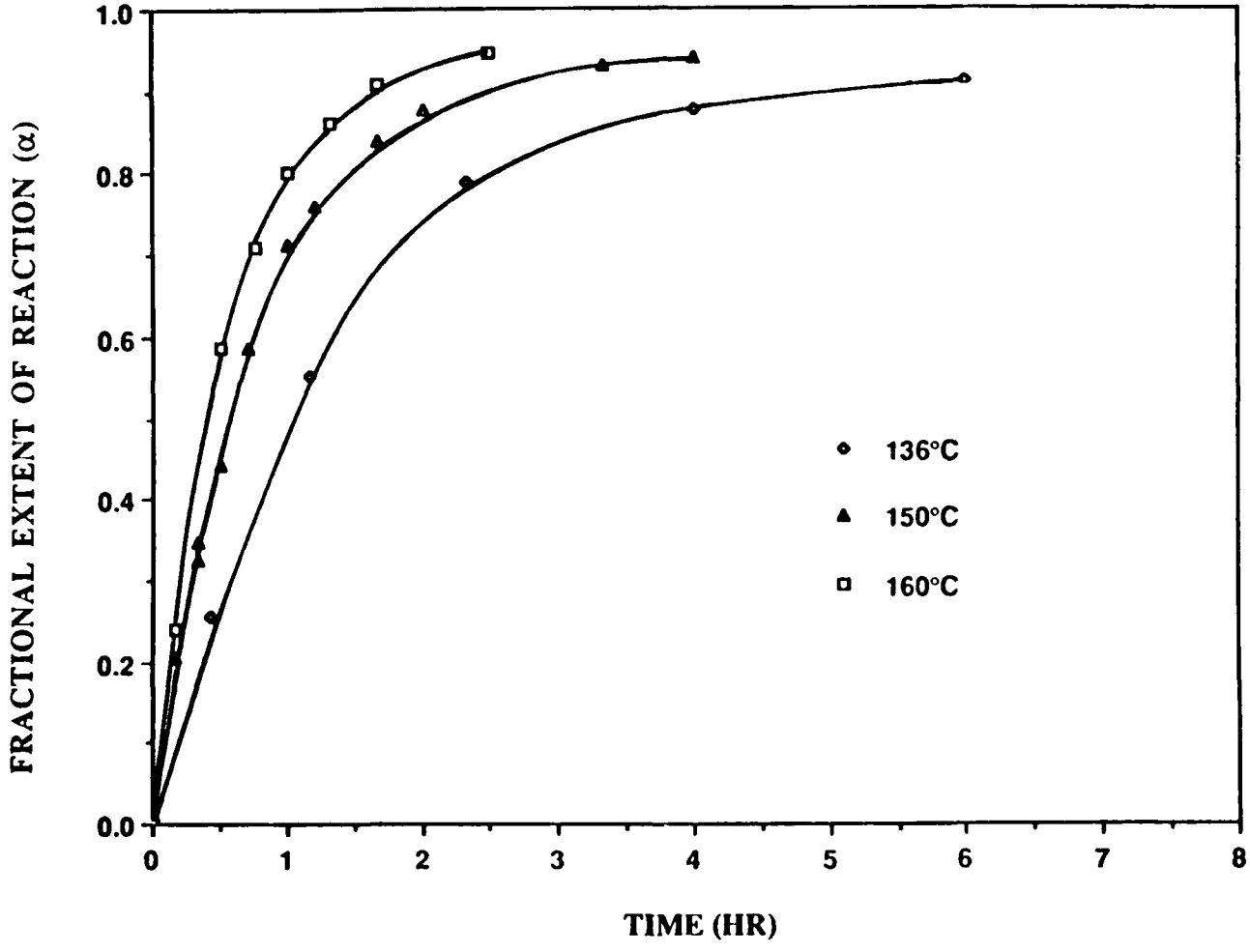


FIGURE 5

ARRHENIUS PLOT OF ISO-CONVERSION TIMES

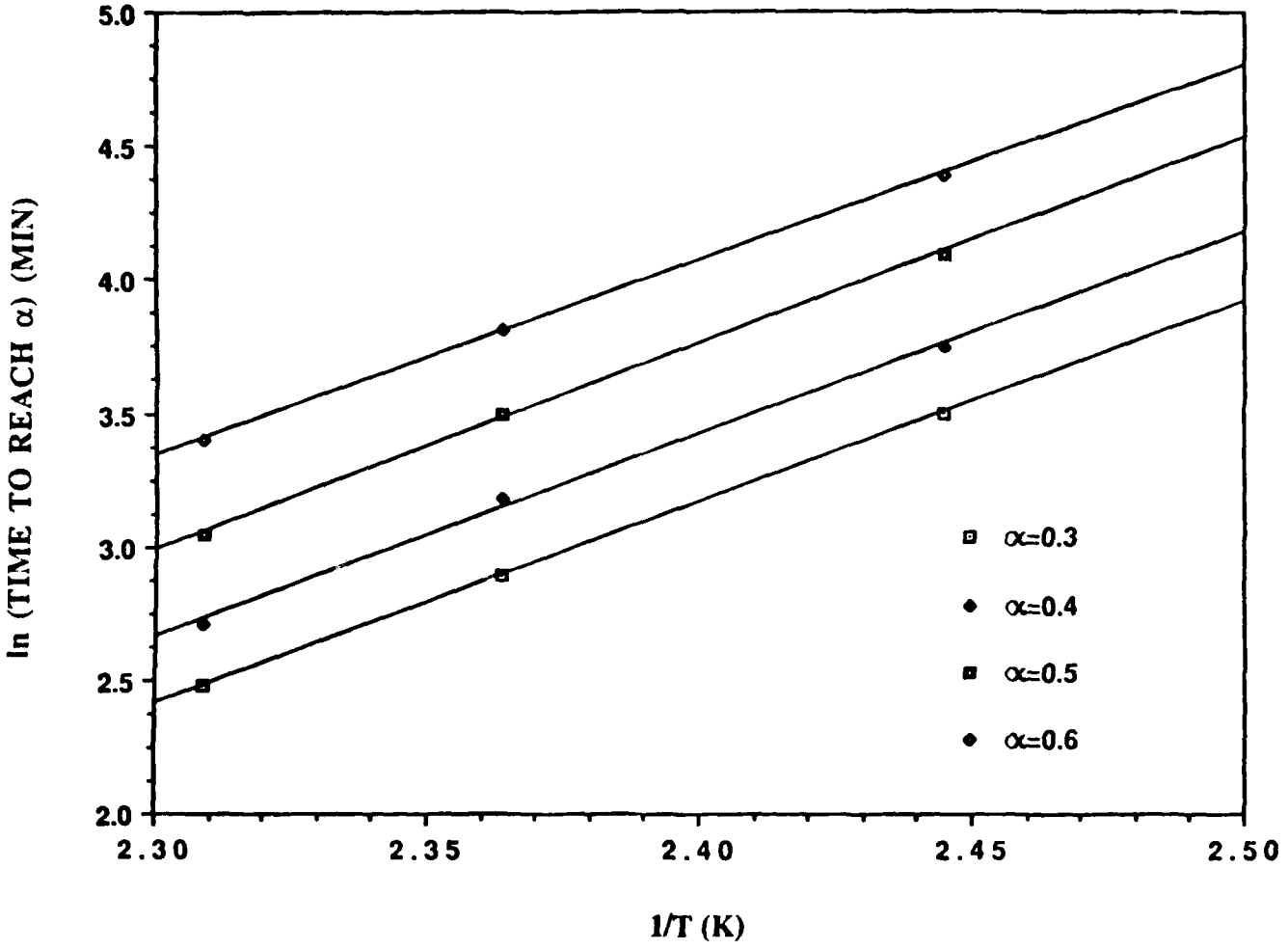


FIGURE 6

DER337/TMAB: FIRST ORDER KINETICS [DSC RESULTS]

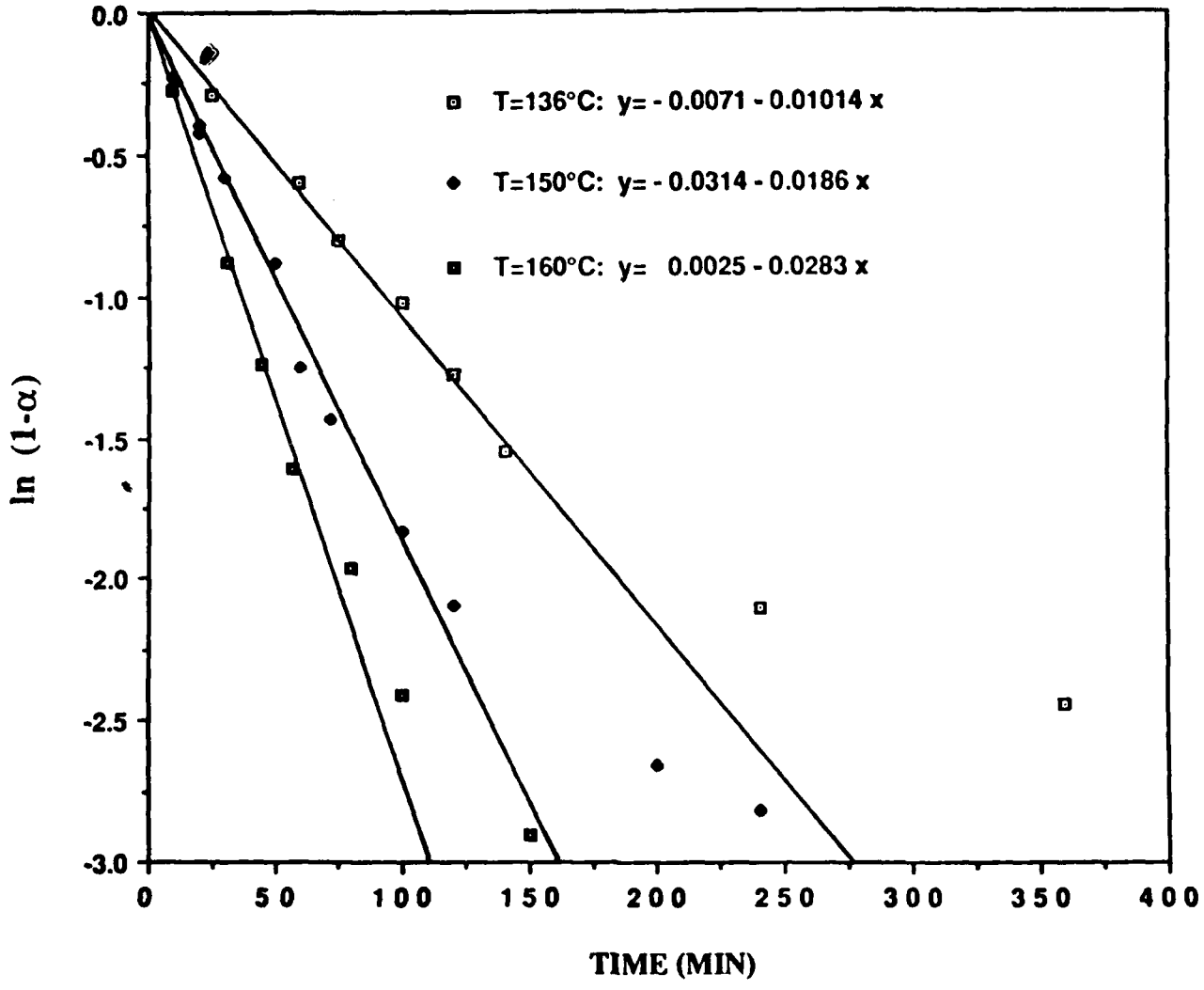


FIGURE 7

ACTIVATION ENERGY FROM 1ST ORDER KINETICS

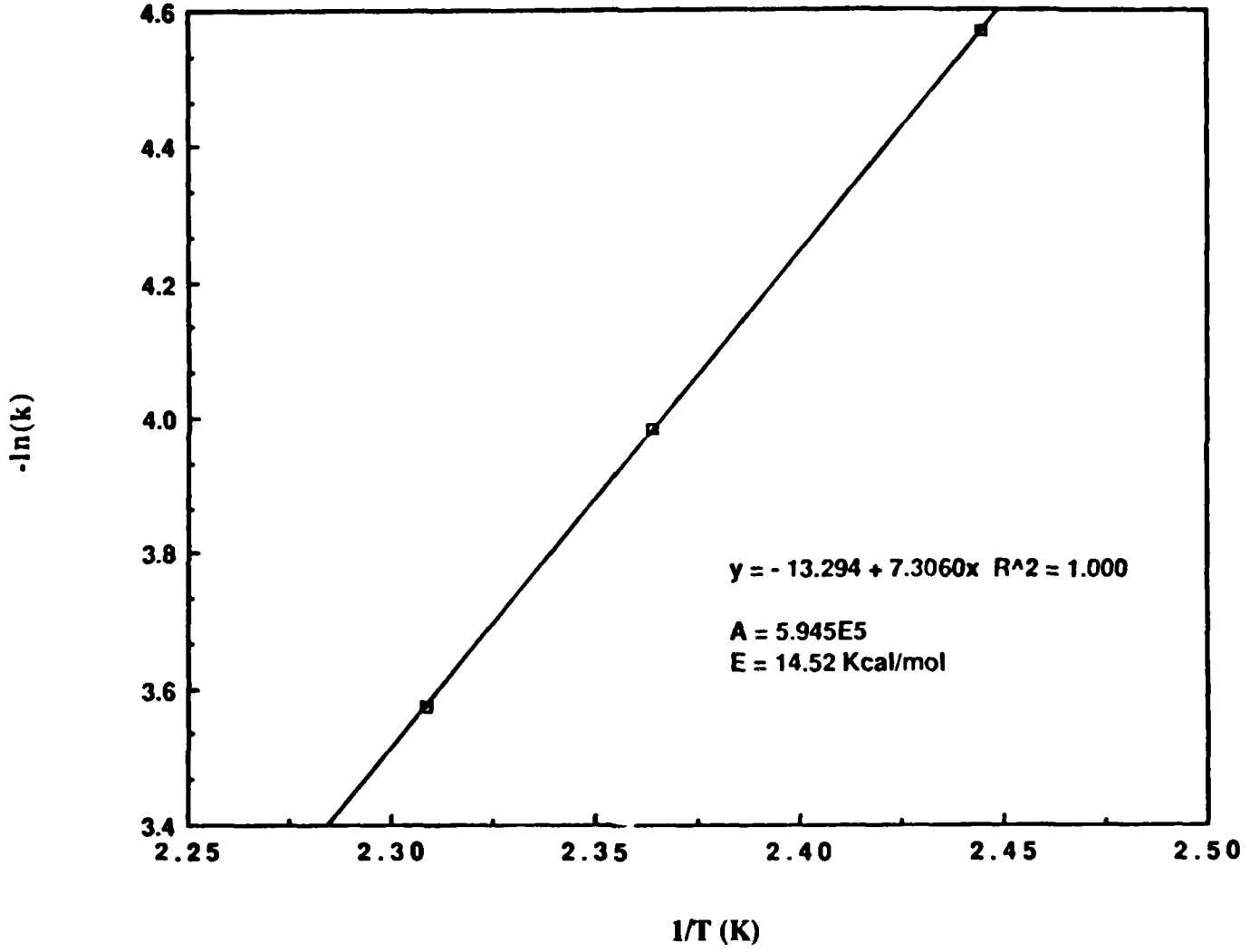


FIGURE 8

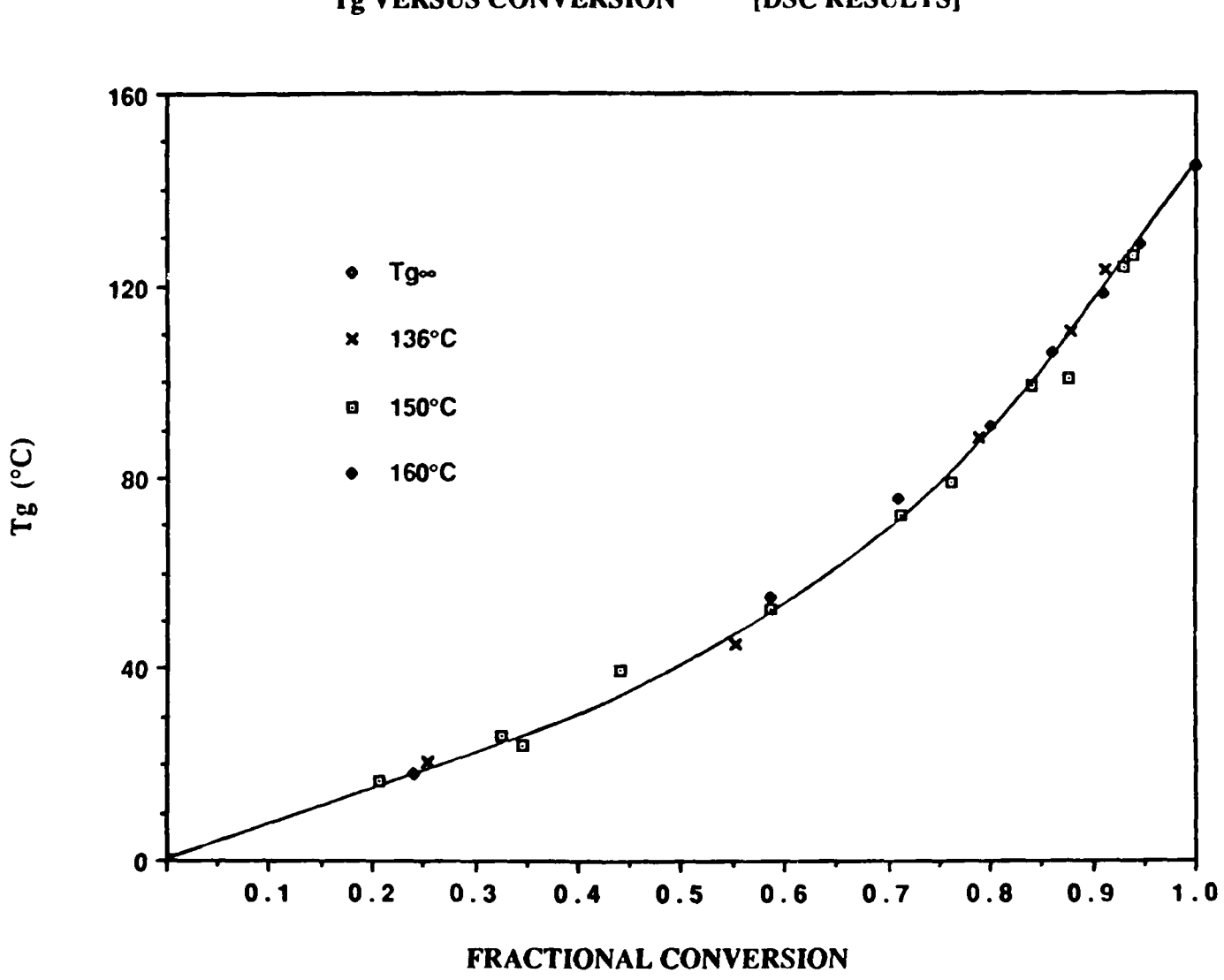

Tg VERSUS CONVERSION [DSC RESULTS]
160
120
80
40
0
Tg (°C)
Tg∞
136°C
150°C
160°C
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
FRACTIONAL CONVERSION

FIGURE. 9

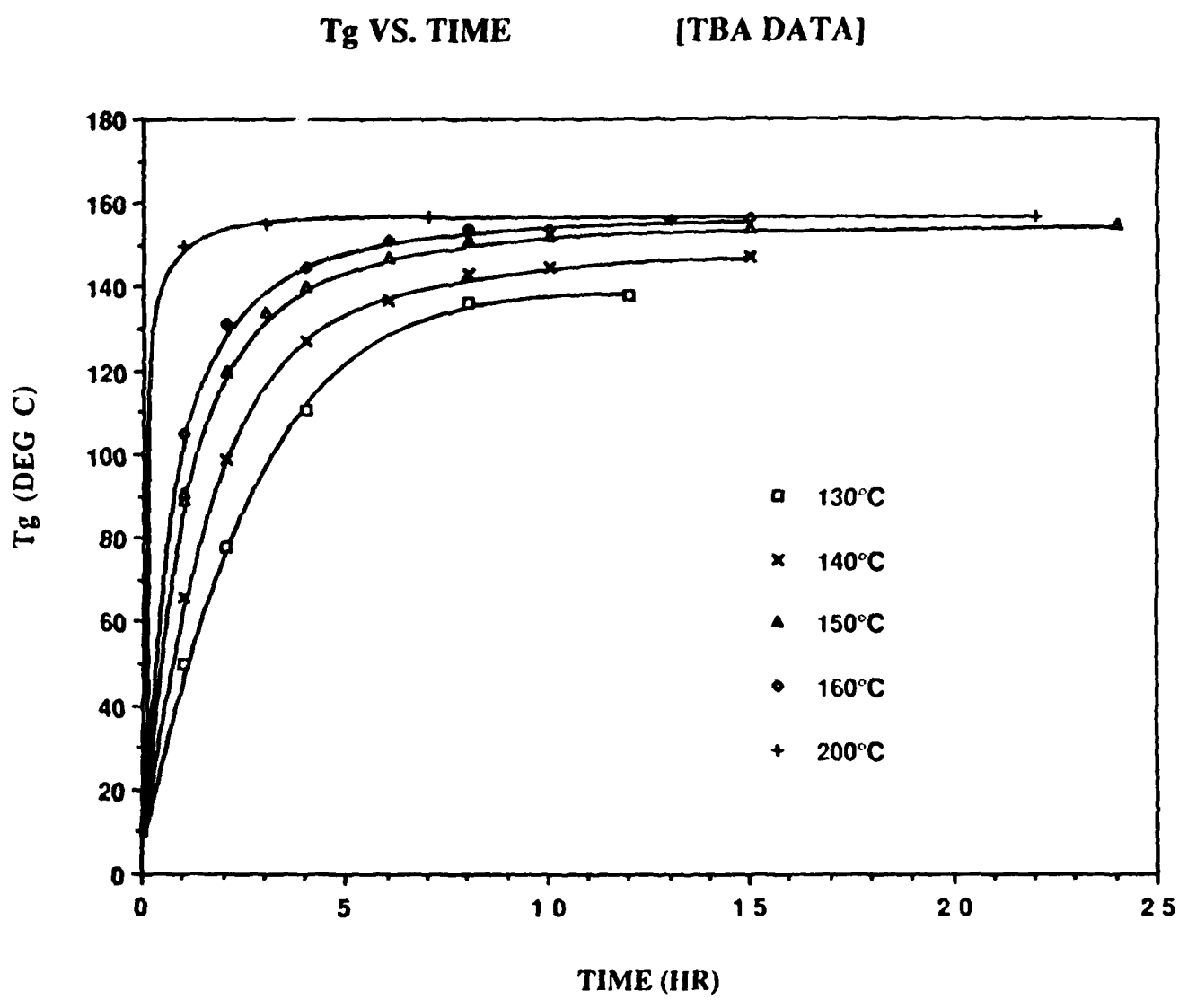

Tg VS. TIME [TBA DATA]
Tg (DEG C)
180
160
140
120
100
80
60
40
20
0
0
5
10
15
20
25
TIME (HR)
130°C
140°C
150°C
160°C
200°C

FIGURE 10

ARREHNIUS PLOT OF ISO-Tg TIMES AND GELATION TIMES

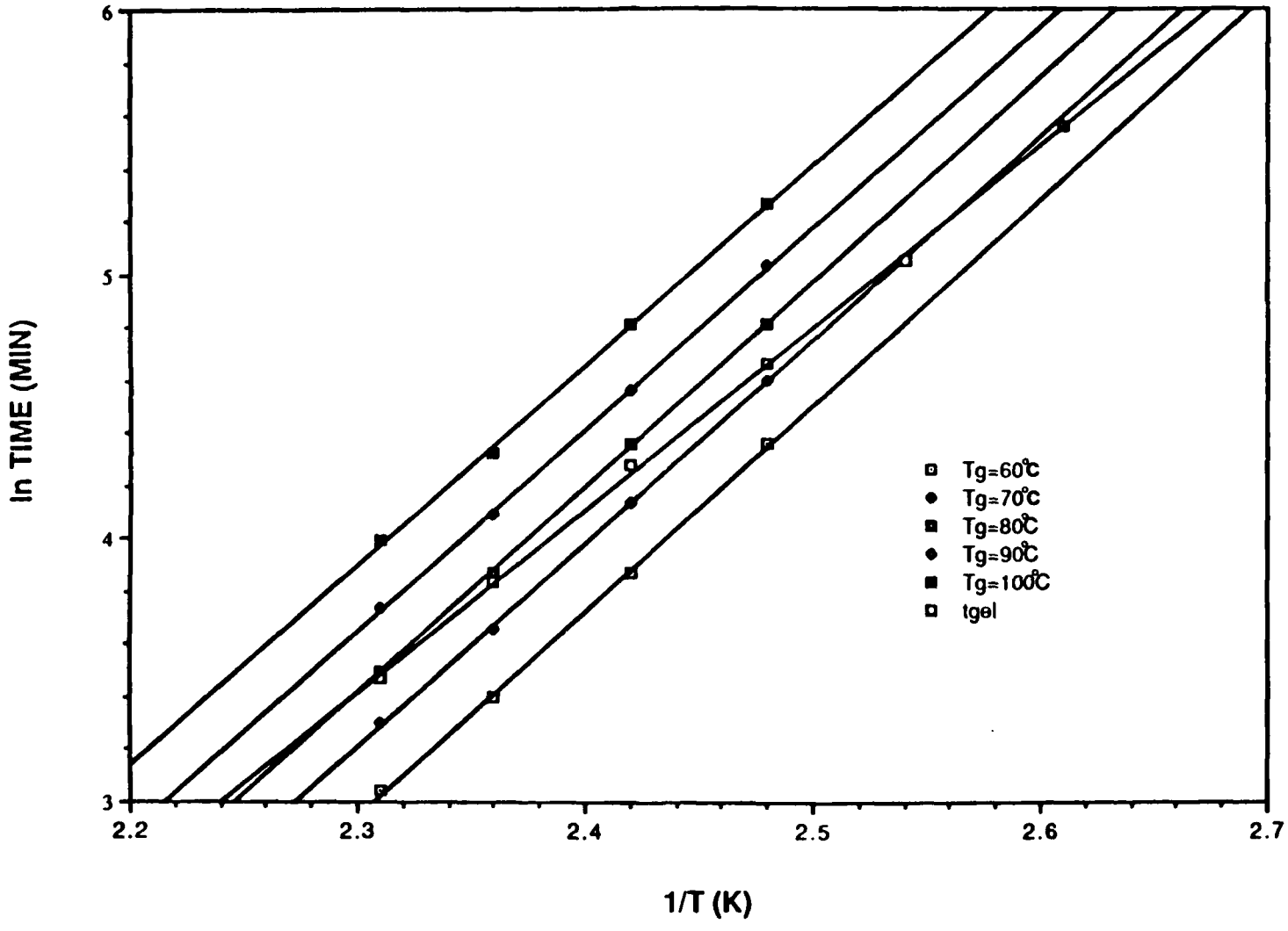


FIGURE 11

TTT DIAGRAM: ISO-Tg, GELATION & VITRIFICATION

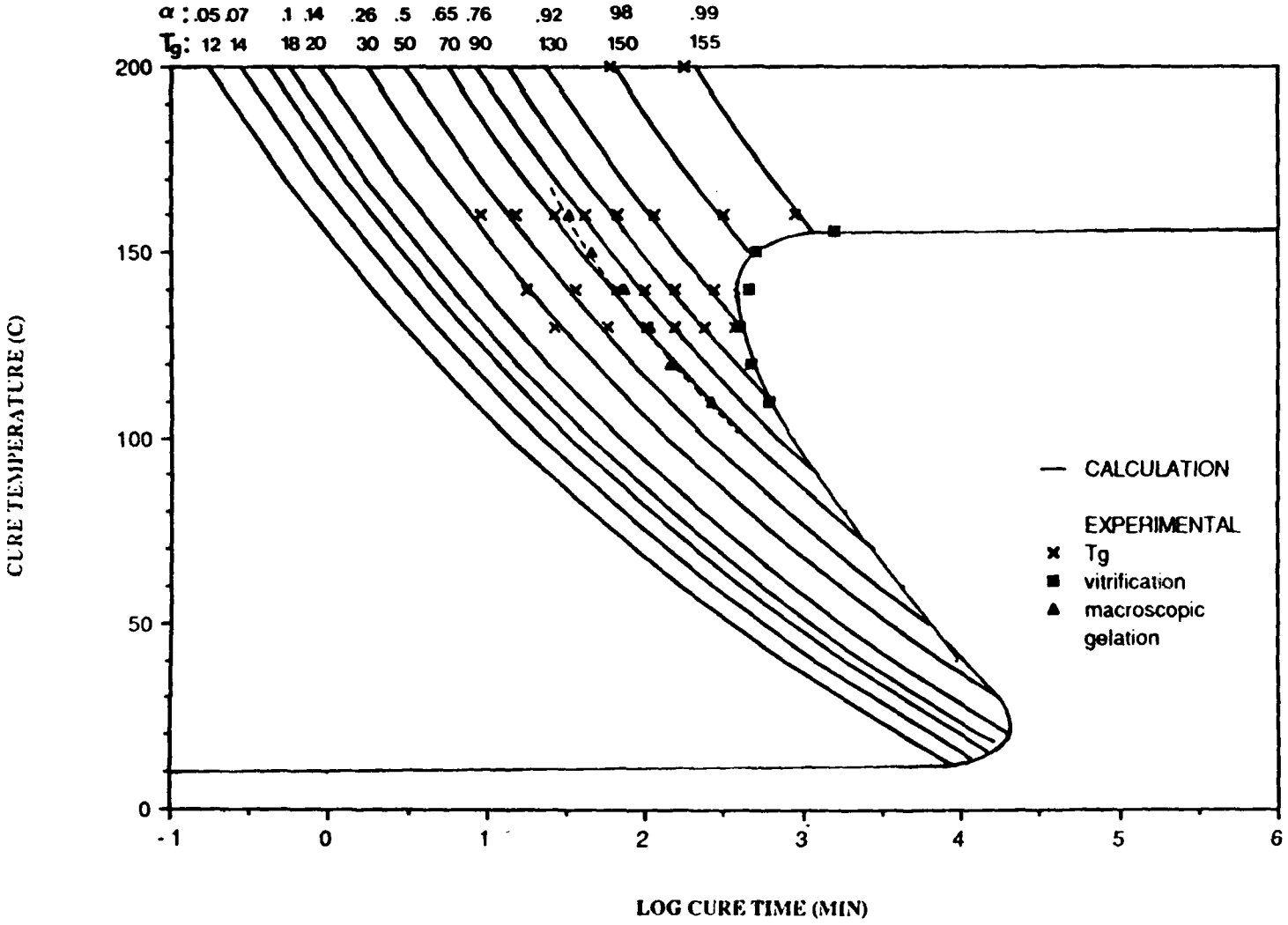


FIGURE 12

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